Lattice mechanics of divalent-metal carbonates

R. K. Singh and N. K. Gaur

School of Physics, Bhopal University, Bhopal 462 026, Madhya Pradesh, India
and Centre for Science and Technology Development Studies, Bhopal 462 016, Madhya Pradesh, India

S. L. Chaplot

Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, Maharashtra, India
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We have investigated the lattice mechanics of $MnCO_3$, $FeCO_3$, and $NiCO_3$, for the first time, using a rigid-molecular-ion model which has been found to be adequately suitable for such descriptions for the calcite-structure crystals [Phys. Rev. B **35**, 4462 (1987)]. The values of cohesive energy calculated by us for these crystals have shown reasonably good agreement with the corresponding thermochemical data. The trend followed by their phonon dispersion curves (PDC's) seems to be realistic as they have close resemblance with the measured PDC's of their counterparts ($NaNO_3$ and $CaCO_3$) belonging to the calcite family.

In recent years, we have described the lattice mechanics of complex molecular calcite crystals [$CaCO_3$, $MgCO_3$, and $ZnCO_3$ (all in Ref. 1) and $LiNO_3$, $NaNO_3$, $AgNO_3$, and $RbNO_3$ (all in Refs. 2 and 3)] satisfactorily by means of a rigid-molecular-ion model (RMIM).[4] This model has been developed by introducing the external mode formalism[5] in the framework of an interaction potential which is modeled by rigid molecular ions attracting each other electrostatically and held apart by some particular exponential short-range repulsion.[4] A lucid description of this model and its applications has been presented elsewhere by Rao *et al.*[4] and by us.[1,2] Motivated from the considerable success of RMIM,[4] we thought it pertinent to investigate the lattice statics and dynamics of the divalent metal carbonates, $MnCO_3$, $FeCO_3$, and $NiCO_3$, in order to complete such investigations for the molecular crystals of calcite family.

Like other members of the calcite family, $MnCO_3$, $FeCO_3$, and $NiCO_3$ possess rhombohedral structure having D_{3d}^6 ($R\bar{3}c$) space group with two molecular formula units per unit cell. The details of their structure have been worked out by Wyckoff[6] and reported elsewhere by Cowley[7] and Rao *et al.*[8] Their unit cell dimensions (a_0, α) and atomic coordinates[6] have been listed in Table I. Using these input data and the computer program DISPR developed by one of us,[9] we have computed the model parameters [effective radii (R_{Kk}) and effective charge (Z_{Kk})] of RMIM and listed them in Table II. It is interesting to note that the ionic radii for C^{4+} and O^{2-} predicted from RMIM are closer to their experimental values.[10] However, the magnitudes of ionic radii of Mn^{2+}, Fe^{2+}, and Ni^{2+} are not so close to their experimental values, but they have followed the observed decreasing trend. The values of the calculated cohesive energies and unit-cell volumes of the molecular crystals under consideration have also been presented in the same Table II.

We have computed the phonon frequencies (ν) corresponding to each wave vector (q) along the [qqq] direction of the Brillouin zone by solving the dynamical equa-

TABLE I. Unit-cell size and atomic positions of divalent metal carbonates (Wyckoff, Ref. 6).

Crystals	a_0 (Å)	α	u	Atomic Positions	
$MnCo_3$	5.905	47°43′	0.27	Mn, Fe, or Ni:	$(0,0,0); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
				C:	$\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$
				O:	$\pm(u + \frac{1}{4}, \frac{1}{4} - u, \frac{1}{4})$
					$\pm(\frac{1}{4} - u, \frac{1}{4}, u + \frac{1}{4})$
					$\pm(\frac{1}{4}, u + \frac{1}{4}, \frac{1}{4} - u)$
$FeCo_3$	5.795	47°45′	0.27		
$NiCo_3$	5.580	48°40′	0.27		

TABLE II. Potential parameters and cohesive energies of divalent metal carbonates.

| Crystals | Ions | Potential Parameter | | Cohesive energy ϕ (kcal/mol)[b] | Unit-cell volume (Å^3) |
		Effective radii (Å)[a]	Effective charge (esu)		
$MnCO_3$	Mn^{2+}	1.20 (0.80)	1.75	$\phi_{Coul} = -880.71$	103.17
	C^{4+}	0.80 (0.77)	0.65	$\phi_{SR} = 53.04$	
	O^{2-}	1.35 (1.46)	-0.80	$\phi_{total} = -827.67$ (-728)	
$FeCO_3$	Fe^{2+}	1.05 (0.76)	1.60	$\phi_{Coul} = -996.24$	97.63
	C^{4+}	0.80 (0.77)	0.80	$\phi_{SR} = 53.37$	
	O^{2-}	1.35 (1.46)	-0.80	$\phi_{total} = -942.87$ (-746)	
$NiCO_3$	Ni^{2+}	0.98 (0.72)	1.85	$\phi_{Coul} = -1053.45$	89.95
	C^{4+}	0.80 (0.77)	0.55	$\phi_{SR} = 76.53$	
	O^{2-}	1.35 (1.46)	-0.80	$\phi_{total} = -976.92$ (-788.76)	

[a]The values enclosed within parentheses are those reported by Kittel (Ref. 10).
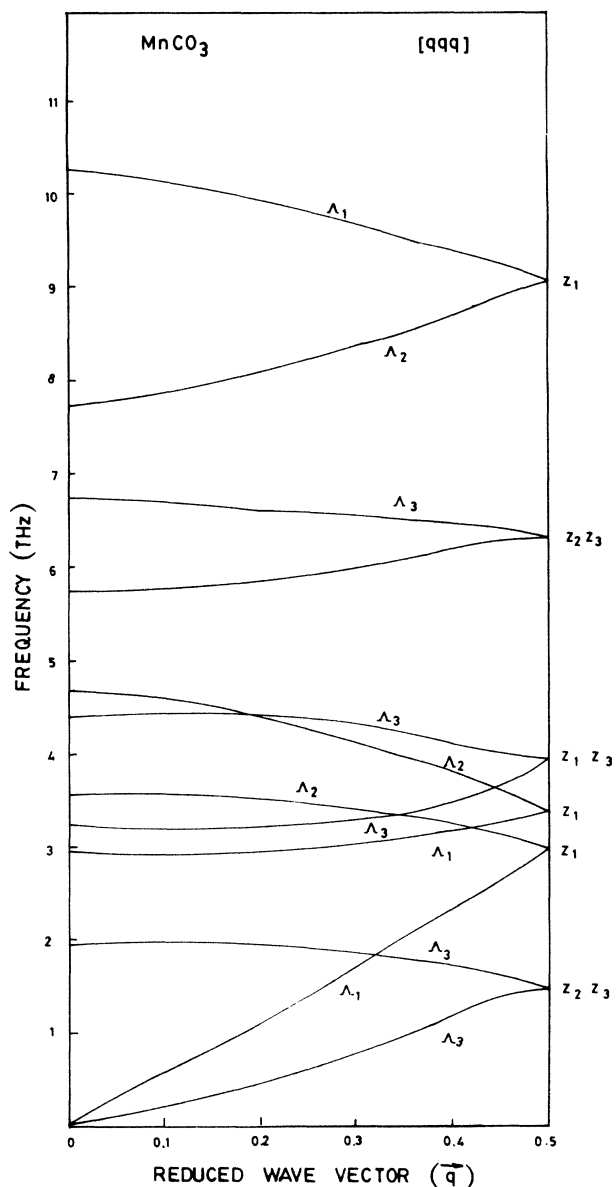[b]The values enclosed within parentheses are measured data (Ref. 11).

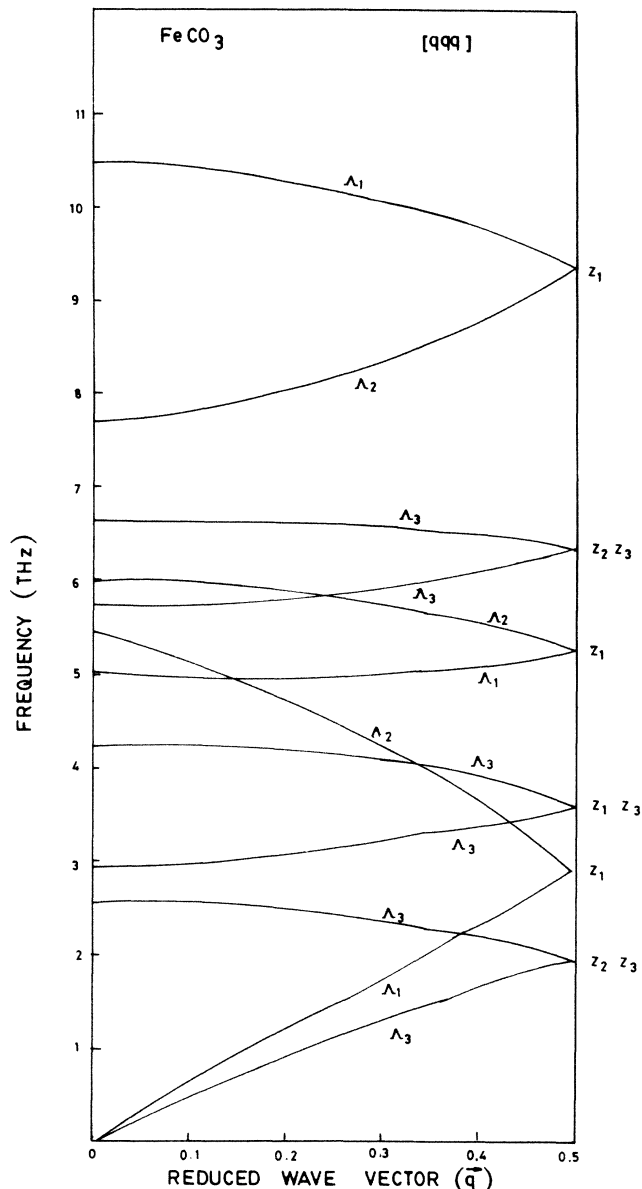FIG. 1. Phonon dispersion curves of $MnCO_3$ obtained from RMIM.

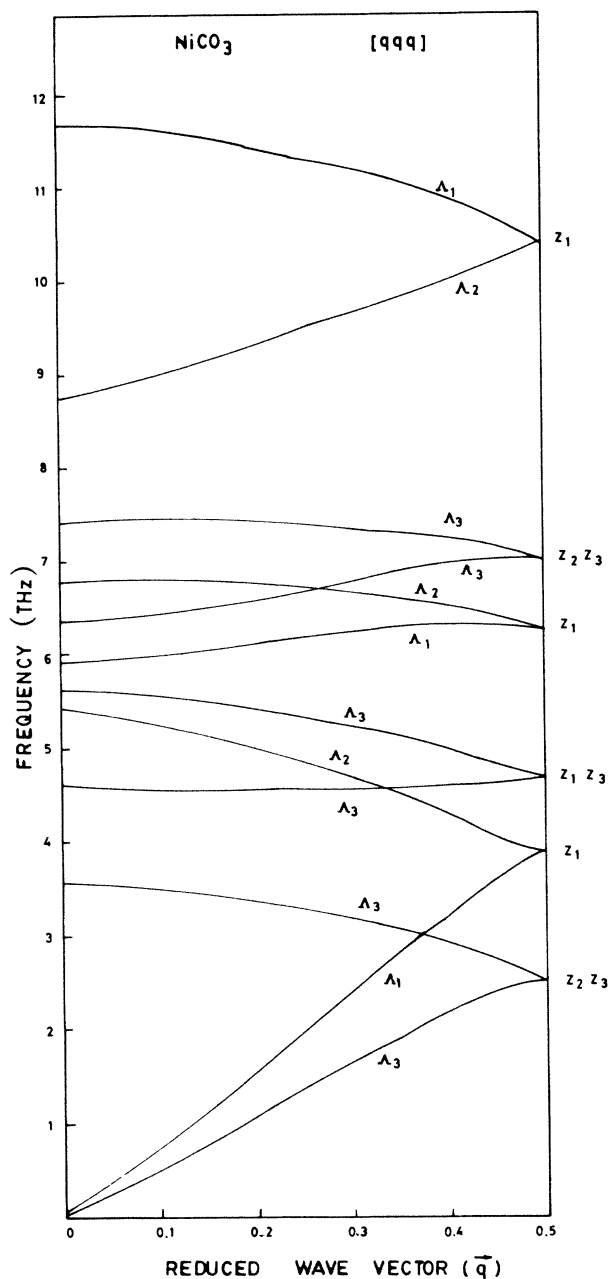FIG. 2. Phonon dispersion curves of $FeCO_3$ obtained from RMIM.

FIG. 3. Phonon dispersion curves of $NiCO_3$ obtained from RMIM.

ly. It is seen from these figures that the phonon branches Λ_1 and Λ_2 meet at the zone boundary and the pairs of frequencies Λ_3 meet at the zone boundary. This conjunction of pairs of branches at the zone boundary is due to the lattice symmetry in divalent-metal carbonates belonging to the same space group.[8]

Using the same set of model parameters, we have computed the cohesive energies for these crystals and compared them with the available thermochemical cycle data.[11] The values of cohesive energies and their contributions from the long-range Coulomb and the short-range repulsive interactions are listed in Table II.

It is interesting to note that our PDC's have followed a systematic trend and exhibited features more or less similar to those revealed by the measured PDC's available only for $CaCO_3$ (Ref. 12) and $NaNO_3$ (Ref. 13). Our results on PDC's are only of academic interest at present but they will certainly serve as a guide to experimental workers in the future. It is also obvious from Figs. 1–3 that at the point Z there exist only two dimensional representations, Z_1, Z_2, Z_3, out of which Z_2 and Z_3 have complex conjugate character. Also, the phonon states of type (Z_2, Z_3) are fourfold degenerate owing to the presence of additional time reversal symmetry.

The values of cohesive energies reported in Table II, although not in very good agreement, have followed a systematic trend and are consistent with their increasing magnitudes in going from $MnCO_3$ to $NiCO_3$ as shown by thermochemical cycle data.[11] It is also seen that the contribution from the short-range overlap repulsion is almost 10% of the total cohesive energy. This feature is indicative of the fact that the major contribution to cohesion on $MnCO_3$, $FeCO_3$, and $NiCO_3$ is due to the Coulomb attraction, just as in the cases of ionic crystals and alkali halides.[14]

A successful description of lattice dynamics and statics achieved here and elsewhere[1-3] for such a complicated system ($MnCO_3$, $FeCO_3$, and $NiCO_3$) appears to be remarkable, bearing in mind the inherent simplicity of RMIM and its less parametric nature. The results of the present investigation can be further improved by incorporating the effects of covalent bond interaction,[15] like angle bending, three-body interaction, and two-body bond-stretching interactions.[14]

tion following the procedure prescribed in the DISPR program.[9] The phonon dispersion curves (PDC's) for $MnCo_3$, $FeCO_3$, and $NiCO_3$ have been obtained by plotting these frequencies against the wave vectors along the Λ direction and depicted in Figs. 1, 2, and 3, respectively.

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